

PTO 09-5606

CC = WO
2001101
A1
0181508

FLEXIBLE PROCESS FOR PRODUCING OIL BASES WITH A ZSM-48 ZEOLITE
[Procédé flexible de production de bases huiles avec une zeolithe zsm-48]

Eric Benazzi et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. JUNE 2009
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY	(19):	WO
DOCUMENT NUMBER	(10):	0181508
DOCUMENT KIND	(12):	A1
PUBLICATION DATE	(43):	2001101
APPLICATION NUMBER	(21):	PCT/FR01/01221
APPLICATION DATE	(22):	20010420
INTERNATIONAL CLASSIFICATION ⁷	(51):	C 10 G 65/12
PRIORITY COUNTRY	(30):	FR
PRIORITY NUMBER	(30):	0005214
PRIORITY DATE	(30):	20000421
INVENTORS	(72):	Eric Benazzi et al.
APPLICANT	(71):	INSTITUT FRANCAIS DU PETROLE [FR/FR]
DESIGNATED CONTRACTING STATES		
(national):	(81):	JP, KR, US.
DESIGNATED CONTRACTING STATES		
(regional):	(84)	European Patent (AT, BE, CH, CY, DE, DK, ES,FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE,TR).
TITLE	(54):	FLEXIBLE PROCESS FOR PRODUCING OIL BASES WITH A ZSM-48 ZEOLITE
FOREIGN TITLE	[54A]:	Procédé flexible de production de bases huiles avec une zeolithe zsm-48

The present invention relates to an improved process for manufacturing base oils of very high quality, that is to say which have a high viscosity index (VI), a low aromatic content, good UV stability and a low pour point, from petroleum cuts with a boiling point higher than 340°C, with possible simultaneous production of middle distillates (gas oils, kerosene in particular) of very high quality, that is to say which have a low aromatic content and a low pour point. The process according to the invention uses a catalyst based on ZSM-48 in catalytic dewaxing.

Prior art

High quality lubricants are of prime importance for the suitable operation of modern machines, automobiles, and trucks.

These lubricants are most often obtained by a sequence of refining steps making it possible to improve the properties of a petroleum cut. In particular, treatment of the heavy petroleum fractions with high contents of linear or only slightly branched paraffins is necessary in order to obtain good quality base oils with the best yields possible, by an operation aiming to eliminate the linear or very slightly branched paraffins, from the loads which will be later used as base oils.

In effect, the high molecular weight, linear or very slightly branched paraffins present in the oils lead to high pour points and therefore to congealing phenomena in cases of low temperature use. In order to reduce the pour point values, these unbranched or slightly branched linear paraffins must be completely or partially eliminated.

This operation can be done by extraction using solvents such as toluene/methyl-ethyl ketone or methyl-isobutyl ketone mixtures; one speaks then of methyl ethyl-ketone (MEK) dewaxing or methyl-isobutyl ketone (MIBK) dewaxing. However, these techniques are expensive, are not always easy to implement and lead to the formation of byproducts, the crude paraffins.

^{*} [Numbers in right margin indicate pagination of the original text.]

Another means is catalytic treatment in the presence or absence of hydrogen, and given the shape selectivity of the zeolites, they are among the most used catalysts.

Catalysts based on zeolites such as ZSM-5, ZSM-11, ZSM-12, ZSM22, ZSM-23, ZSM-35 AND ZSM-38 have been described for their use in these processes.

Object of the invention

The applicant directed his research efforts to the development of an improved process for manufacturing very high quality lubricating oils.

The present invention therefore relates to a sequence of processes for the joint manufacturing of very high quality base oils and very high quality middle distillates (gas oils in particular). The oils obtained have a high viscosity index (VI), a low aromatic content, low volatility, good UV stability and a low pour point, from petroleum cuts with a boiling point higher than 340°C.

In particular, and contrary to the usual sequences of processes or those coming from the earlier state of the art, this process is unlimited in the quality of the oil products that can be obtained by it; in particular, a wise choice of the conditions of operation makes it possible to obtain medicinal grade white oils (that is to say with excellent qualities). More precisely, the invention relates to a process for the production of high quality oils and possibly of high quality middle distillates from a hydrocarbon load of which at least 20 volume % boils at above 340°C, a process which successively entails the following steps:

- (a) hydrotreatment carried out at a temperature of 330-450°C, under a pressure of 5-25 MPa, with a space velocity of $0.1-6 \text{ h}^{-1}$, in the presence of hydrogen in a hydrogen/hydrocarbon volume ratio of 100-2,000, and in the presence of an amorphous catalyst containing at least one metal of group VIII and at least one metal of group VI B,

- (b) hydrocracking, without intermediate separation of the effluent obtained after the hydrotreatment, the hydrocracking being carried out at a temperature of 340-430°C, under a pressure of 5-25 MPa, with a space velocity of 0.1-5 h⁻¹, in the presence of hydrogen, and in the presence of a catalyst containing at least one zeolite and also containing at least one element of group VIII and at least one element of group VI B,
- (c) atmospheric distillation of the effluent obtained after hydrocracking in order to separate the gases from the liquid,
- (d) catalytic dewaxing of at least one liquid fraction obtained by atmospheric distillation and which contains compounds with a boiling point higher than 340°C, dewaxing at a temperature of 200-500°C, under a total pressure 1-25 MPa, with a velocity per unit of volume and per hour of 0.05-50 h⁻¹, with 50-2000 L of hydrogen/L of load, in the presence of a catalyst containing a zeolite chosen from the group formed by the ZSM-48, EU-12, EU-11 AND ZBM-30 zeolites,
- (e) the dewaxed effluent directly undergoes a hydrofinishing treatment carried out at a temperature of 180-400°C, which is lower than the temperature of the catalytic dewaxing by at least 20°C and at most 200°C, under a total pressure of 1-25 MPa, with a velocity per unit of volume and per hour of 0.05-100 h⁻¹, in the presence of 50-2000 L of hydrogen/liter of load, and in the presence of an amorphous catalyst for the hydrogenation of the aromatics, containing at least one metal chosen from the group of the metals of group VIII and the metals of group VI B,
- (f) the effluent coming from the hydrofinishing treatment undergoes a distillation step entailing an atmospheric distillation and a vacuum distillation so as to separate at least one oil fraction with a boiling point higher than 340°C, and which has a pour point lower than -10°C, a weight content of aromatic compounds less than 2%, and a VI greater than 95, a viscosity at 100°C of at least

/3

3 cSt (or 3 mm²/s), and so as to separate possibly at least one middle distillate fraction with a pour point lower than or equal to -20°C, an aromatic content of at most 2 wt% and a polyaromatic content of at most 1 wt%.

Detailed description of the invention

The process according to the invention includes the following steps:

Step (a): Hydrotreatment

The hydrocarbon load from which the oils and possibly the middle distillates of high quality are obtained contains at least 20 volume % boiling at above 340°C.

/4

Quite varied loads can therefore be treated by the process.

The load can, for example, be LCO (light cycle oil), vacuum distillates coming from the direct distillation of the crude or from conversion units such as FCC, the coker or viscoreduction units, or coming from aromatic extraction units, or coming from desulfuration or hydroconversion of RAT (atmospheric residues) and/or of RSV (vacuum residues), or else the load can be a deasphalted oil, or any mixture of the loads mentioned in the preceding. The list above is not limiting. In general, the loads suitable for the objective oils have an initial boiling point higher than 340°C and better yet higher than 370°C.

In a first step, the load undergoes hydrotreatment, during which it is put in contact, in the presence of hydrogen, with at least one catalyst entailing an amorphous support and at least one metal having a hydro-dehydrogenating function which is provided, for example, by at least one element of group VI B and at least one element of group VIII, at a temperature between 330 and 450°C, and preferably 360-420°C, under a pressure between 5 and 25 MPa, and preferably lower than 20 MPa, the space

velocity being between 0.1 and 6 h^{-1} , and preferably $0.3\text{-}3\text{ h}^{-1}$, and the quantity of hydrogen introduced is such that the hydrogen/hydrocarbon volume ratio is between 100 and 2000.

During the first step, the use of a catalyst favoring hydrogenation over cracking, used under appropriate thermodynamic and kinetic conditions, makes possible an extensive reduction of the content of condensed polycyclic aromatic hydrocarbons. Under these conditions, the majority of the products containing nitrogen and sulfur of the load are also transformed. This operation therefore makes it possible to eliminate two types of compounds known to be inhibitors of the zeolite catalyst used subsequently in the process.

This first step, by bringing about the pre-cracking of the load to be treated, makes it possible to adjust the properties of the oil base coming out of this first step as a function of the grade of the oil base that one wishes to obtain coming out of the process. Advantageously, it will be possible to perform this adjustment by varying the nature and quality of the catalyst used in the first step and/or the temperature of this first step, so as to raise the viscosity index for the oil base, fraction with a boiling point higher than 340°C , coming out of this step. The viscosity index obtained after dewaxing is preferably between 80 and 150, and more preferably between 90 and 140 or even 90 and 130. /5

The support generally is based on (and preferably consists essentially of) alumina or amorphous silica-alumina; it can also contain boron oxide, magnesia, zirconia, titanium oxide or a combination of these oxides. The hydro-dehydrogenating function is preferably fulfilled by at least one metal or compound of metal of groups VIII and VI preferably chosen from: molybdenum, tungsten, nickel and cobalt.

This catalyst can advantageously contain phosphorus; in effect, it is known in prior art that the compound gives the hydrotreatment catalysts two advantages: ease of preparation particularly during the impregnation with the nickel and molybdenum solutions, and better hydrogenation activity.

The preferred catalysts are NiMo and/or NiW catalysts on alumina, also NiMo and/or NiW catalysts on alumina doped by at least one element included in the group of atoms formed by phosphorus, boron, silicon and fluorine, or else NiMo and/or NiW catalysts on silica-alumina, or on silica-alumina-titanium oxide doped or not by at least one element included in the group of atoms formed by phosphorus, boron, fluorine and silicon.

The total concentration of oxides of metals of groups VI and VIII is between 5 and 40 wt% and preferably between 7 and 30%, and the weight ratio expressed in metal oxide between metal(or metals) of group VI over metal (or metals) of group VIII is preferably between 20 and 1.25 and even more preferably between 10 and 2. The concentration of phosphorus oxide P_2O_5 will be less than 15 wt% and preferably less than 10 wt%.

The product obtained after this first step is sent to a second catalyst in a second step without intermediate separation of ammonia (NH_3) and hydrogen sulfide (H_2S) or distillation.

Step (b): Hydrocracking

The effluent coming from the first step (a) is completely introduced onto the catalyst of the second step (b) in the presence of hydrogen where it is hydrocracked in the presence of a bifunctional catalyst containing a zeolitic acid and a hydro-dehydrogenating metallic function.

/6

During this step, the polyaromatic and polynaphthenoaromatic compounds partially or totally hydrogenated during the first step are hydrocracked on the acid sites leading to the formation of paraffins. These paraffins in the presence of a bifunctional catalyst can undergo isomerization and then possibly hydrocracking leading respectively to the formation of isoparaffins and lighter cracking products.

The conversion of the polyaromatic compounds with several nuclei [rings] requires hydrogenation before their cracking.

The catalyst of the second step contains a zeolite, a support and a hydro-dehydrogenating function.

The hydro-dehydrogenating function is advantageously obtained by a combination of metals of groups VI B (for example, molybdenum and/or tungsten) and/or metals of group VIII preferably not noble metals (for example, cobalt and/or nickel) of the periodic classification of the elements. Preferably, this catalyst can also contain at least one promoter element deposited on the surface of the catalyst, an element which is included in the group formed by phosphorus, boron and silicon and advantageously phosphorus.

The total concentration of metals of groups VI B and VIII, expressed in metal oxides with respect to the support, is generally between 5 and 40 wt%, and preferably between 7 and 30 wt%. The weight ratio (expressed in metal oxides) of the metals of group VIII over metals of group VI B is preferably between 0.05 and 0.8, and preferably between 0.13 and 0.5.

This type of catalyst can advantageously contain phosphorus, the content of which, expressed in phosphorus oxide P_2O_5 with respect to the support, will generally be less than 15 wt%, and preferably less than 10 wt%.

The boron and silicon contents are less than 15 wt% and preferably less than 10 wt% (expressed in oxide).

The amorphous or poorly crystallized support is chosen from the group formed by alumina, silica, silica alumina, alumina-boron oxide, magnesia, silica-magnesia, zirconia, titanium oxide, clay, alone or in mixtures.

The zeolite is advantageously chosen from the group formed by zeolite Y (FAU faujasite structural type) and Beta zeolite (BEA structural type) according to the nomenclature developed in "Atlas of

/7

zeolites structure types", W.M. Meier, D.H. Olson and Ch. Baerlocher, 4th revised Edition 1996, Elsevier.

The zeolite weight content is between 2 and 80% and preferably between 3 and 50% with respect to the final catalyst, and advantageously between 3-25%.

The zeolite can possibly be doped by metallic elements such as, for example, metals of the family of the rare earths, particularly lanthanum and cerium, or noble or non-noble metals of group VIII, such as platinum, palladium, ruthenium, rhodium, iridium, iron and other metals such as manganese, zinc, magnesium.

A particularly advantageous acidic HY zeolite is characterized by different specifications: a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ between approximately 6 and 20 and preferably between approximately 12 and 50; a sodium content less than 0.15 wt% determined based on the zeolite calcined at 1100°C; a lattice parameter a of the unit cell between 24.58×10^{-10} m and 24.24×10^{-10} m and preferably between 24.38×10^{-10} m and 24.26×10^{-10} m; a sodium ion uptake capacity CNa , expressed in grams of Na per 100 grams of zeolite modified, neutralized and then calcined, greater than 0.85; a specific surface area determined by the B.E.T. method greater than approximately 400 m^2/g and preferably greater than 550 m^2/g , a water vapor absorbency at 25°C for a partial pressure of 2.6 torr (or 34.6 MPa), greater than approximately 6%, a pore distribution, determined by nitrogen physisorption, between 5 and 45% and preferably between 5 and 40% of the total pore volume of the zeolite contained in pores of diameter situated between 20×10^{-10} m and 80×10^{-10} m, and between 5 and 45% and preferably between 5 and 40% of the total pore volume of the zeolite contained in pores of diameter greater than 80×10^{-10} m and generally less than 1000×10^{-10} m, the rest of the pore volume being contained in the pores of diameter less than 20×10^{-10} m.

The preferred catalyst essentially contains at least one metal of group VI, and/or at least one non-noble metal of group VIII, a zeolite Y and alumina.

An even more preferred catalyst essentially contains nickel, molybdenum, a zeolite Y as defined in the preceding and alumina.

The conditions of operation under which this second step (b) is carried out are important.

The pressure will be kept between 5 and 25 MPa, advantageously between 5 and 20 MPa, and preferably between 7 and 15 MPa; the space velocity will be between 0.1 h^{-1} and 5 h^{-1} and preferably between 0.5 h^{-1} and 4.0 h^{-1} .

The temperature is adjusted in the second step (b) so as to obtain the desired viscosity and VI. It is between 340 and 430°C , and in general it is advantageously situated between 370 and 420°C .

These two steps (a) and (b) can be carried out using the two types of catalysts in (two or more) different reactors, or preferably in at least two catalyst beds installed in the same reactor.

The hydrogen is separated from the effluent coming out of the hydrocracker; the effluent then directly undergoes atmospheric distillation (step c) so as to separate the gases that form (such as ammonia and hydrogen sulfide (H_2S), as well as the other light gases that would be present, hydrogen possibly...). At least one liquid fraction containing products whose boiling point is higher than 340°C is obtained.

Distillation at atmospheric pressure can advantageously be carried out in order to obtain several fractions (gasoline, kerosene, gas oil, for example), with a boiling point of at most 340°C and a fraction (called residue) with an initial boiling point higher than 340°C (and preferably higher than 370°C).

This fraction has a VI, before dewaxing, between 95 and 165 and preferably at least 110.

According to the invention, this fraction (residue) will then be treated in the catalytic dewaxing step, that is to say without undergoing vacuum distillation.

In a variant of the process, the residue, before being catalytically dewaxed, undergoes extraction of the aromatic compounds (constituting step (c')). This extraction is carried out by any known means; the solvents most used are furfural and N-methylpyrrolidone.

The naphthenoaromatic compounds are thus extracted, and the raffinate obtained has a viscosity index greater than that of the residue going into the extraction step. Through this operation, the VI of the product obtained after the hydrofinishing step is further increased.

In another embodiment oriented more towards the objective of production of middle distillates, the cut point is lowered, and instead of cutting at 340°C as in the preceding, it will be possible, for example, to include the gas oils and possibly the kerosenes in the fraction containing the compounds boiling at above 340°C. For example, a fraction with an initial boiling point of at least 150°C is obtained.

In contrast, the residue can undergo extraction of the aromatic compounds before being catalytically dewaxed. This extraction is carried out by any known means, furfural being used most often. The usual conditions of operation are used.

The raffinate obtained has a viscosity index greater than the index of the residue going in. The VI of the product obtained after hydrofinishing is thus further increased.

The fraction thus obtained, which contains said compounds, will be treated directly by catalytic dewaxing; the other fractions (150°C) are or are not treated separately by catalytic dewaxing, in this embodiment.

Generally, called middle distillates in this text is (are) the fraction(s) with an initial boiling point of at least 150°C and a final boiling point ranging up to below the residue, that is to say generally up to 340°C or preferably 370°C.

An advantage of this conversion process that is described (hydrotreatment and hydrocracking, therefore using a zeolite type catalyst) is that it generally makes it possible manufacture lubricating oil

bases with a viscosity greater than that obtained by an amorphous catalyst with the same conversion. In the course of the hydrocracking process, the viscosity at 100°C of the non-converted fraction with boiling point higher than 340°C and preferably higher than 370°C, is a decreasing function of the conversion level obtained. /10

When this conversion level is high (beyond 70%), the viscosity of the residue obtained with an amorphous catalyst is such that it cannot be used for producing the more viscous grades of lubricating oils (500 N and Bright Stock). This limitation disappears when the zeolite catalyst described above is used.

Thus, the ratio between the viscosity at 100°C of the 370°C+ hydrocracking residue obtained by a process using only non-zeolitic catalysts (V_{100A}) and the viscosity at 100°C of the 370°C+ hydrocracking residue obtained by our process (V_{100Z}) and with the same conversion, this ratio (V_{100A}/V_{100Z}) is strictly less than 1, and preferably between 0.95 and 0.4.

Step (d): Catalytic hydrodewaxing (HDPC)

Then, at least a portion and preferably all of the fraction containing the compounds boiling at above 340°C, as defined above, coming from the second step and from atmospheric distillation (c) undergoes a catalytic dewaxing step in the presence of hydrogen and a hydrodewaxing catalyst containing an acid function and a hydro-dehydrogenating metallic function and at least one matrix.

Let us note that the compounds boiling at above 340°C always undergo catalytic dewaxing.

The acid function is provided by at least one zeolite chosen from the group formed by the ZSM-48, EU-2, EU-11 and ZBM-30 zeolites.

The use of said zeolites in particular makes it possible to produce products with a low pour point and a high viscosity index with good yields in the context of the process according to the invention.

The molecular sieve weight content in the hydrodewaxing catalyst is between 1 and 90%, preferably between 5 and 90% and even more preferably between 10 and 85%.

The matrixes used for executing the forming the catalyst are, for example and in a non-limiting manner, the alumina gels, the aluminas, magnesia, the amorphous silica-aluminas, and their mixtures. Techniques such as extrusion, pelletizing or drageification can be used for carrying out the forming operation. /11

The catalyst also contains a hydro-dehydrogenating function provided, for example, by at least one element of group VIII and preferably at least element included in the group formed by platinum and palladium. The weight content of non-noble metal of group VIII, with respect to the final catalyst, is between 1 and 40% and preferably between 10 and 30%. In this case, the non-noble metal is often associated with at least one metal of group VIB (Mo and W preferred). If it is a matter of a noble metal of group VIII, the weight content, with respect to the final catalyst, is less than 5%, preferably less than 3% and even more preferably less than 1.5%.

In the case of use of noble metals of group VIII, the platinum and/or palladium is (are) preferably located on the matrix, defined as in the above.

The hydrodewaxing catalyst according to the invention can moreover contain 0 to 20 wt% and preferably 0 to 10 wt% (expressed in oxides) phosphorus. The combination of metal(s) of group VI B and/or of metal(s) of group VIII with phosphorus is particularly advantageous.

The hydrocracking residue (that is to say the fraction with an initial boiling point higher than 340°C) obtained in step (c) of the process according to the invention and which is to be treated in this hydrodewaxing step (d), has the following characteristics: it has an initial boiling point higher than 340°C and preferably higher than 370°C, a pour point of at least 15°C, a nitrogen content less than 10 ppm by weight[,] a sulfur content less than 50 ppm by weight or preferably less than 10 ppm by

weight, a viscosity index of 35 to 165 (before dewaxing), preferably at least equal to 110 and even more preferably less than 150, a content of aromatic compounds less than 10 wt%, a viscosity at 100°C greater than or equal to 3 cSt (mm^2/s).

These characteristics are also those of the residue that would be obtained by atmospheric distillation of a sample of a liquid fraction containing the compounds with a boiling point higher than 340°C, said fraction having an initial boiling point lower than or equal to 340°C and undergoing catalytic dewaxing.

The conditions of operation under which the hydrodewaxing step of the process of the invention is carried out are the following: /12

- the reaction temperature is between 200 and 500°C and preferably between 250 and 470°C, and advantageously 270-430°C;
- the pressure is between 0.1 and 25 MPa (10^5 Pa) and preferably between 1.0 and 20 MPa;
- the velocity per unit of volume and per hour (vvh expressed in volume of load injected per unit of volume of catalyst and per hour) is between approximately 0.5 and approximately 50 and preferably between approximately 0.1 and approximately 20 h^{-1} , and even more preferably between 0.2 and 10 h^{-1} .

They are chosen so as to obtain the desired pour point.

The contact between the load going into dewaxing and the catalyst is brought about in the presence of hydrogen. The percentage of hydrogen used and which is expressed in liters of hydrogen per liter of load is between 50 and approximately 2000 L of hydrogen per liter of load and preferably between 100 and 1500 L of hydrogen per liter of load.

The expert in the field knows that improvement of the pour point of oil bases, whether it is obtained by the solvent dewaxing (DPS) process or by a catalytic hydrodewaxing (HDPC) process, brings about a lowering of the viscosity index (VI).

One of the characteristics of the process according to the invention is that:

- the variation of VI in the catalytic hydrodewaxing (HDPC) step is preferably greater than or equal to 0, for a given pour point,

or

- when a reduction of the VI is observed in the catalytic hydrodewaxing (HDPC) step, this lowering is smaller than that which can be observed in the case of solvent dewaxing (DPS) in order to obtain the same pour point. Thus, the ratio between the variation of VI, of the oil base, in the catalytic dewaxing step, and the variation of VI, of the oil base, in the solvent dewaxing step, $\Delta VI_{HDPC} / \Delta VI_{DPS}$ is strictly less than 1 for a given pour point.

Step (e): Hydrofinishing (Hydrofinishing)

/13

All of the effluent coming out of the catalytic hydrodewaxing step, without intermediate distillation, is sent to a hydrofinishing catalyst in the presence of hydrogen so as to bring about thorough hydrogenation of the aromatic compounds which are detrimental to the stability of the oils and of the distillates. However, the acidity of the catalyst must be sufficiently low not to lead to the formation of cracking product with a boiling point lower than 340°C so as not to degrade the final oil yields.

The catalyst used in this step entails at least one metal of group VIII and/or at least one element of group VIB of the periodic classification. The strong metallic functions: platinum and/or palladium, or nickel-tungsten, nickel-molybdenum combinations will advantageously be used for bringing about a thorough hydrogenation of the aromatics.

These metals are deposited and dispersed on a support of amorphous or crystalline oxide type, such as the aluminas, the silicas, the silica-aluminas, for example.

The hydrofinishing (HDF) catalyst can also contain at least one element of group VII A of the periodic classification of the elements. Preferably, these catalysts contain fluorine and/or chlorine.

The weight contents of metals are between 10 and 30% in the case of the non-noble metals and are less than 2%, and preferably between 0.1 and 1.5%, and even more preferably between 0.1 and 1.0% in the case of the noble metals.

The total quantity of halogen is between 0.02 and 30 wt%, advantageously 0.01 to 15%, or 0.01 to 10%, and preferably 0.01 to 5%.

Among the catalysts that can be used in this HDF step and which lead to excellent performances, and particularly for obtaining medicinal oils, it will be possible to mention the catalysts containing at least one noble metal of group VIII (platinum, for example) and at least one halogen (chlorine and/or fluorine), the chlorine and fluorine combination being preferred.

The conditions of operation under which the hydrofinishing step of the process of the invention is carried out are the following: /14

- the reaction temperature is between 180 and 400°C and preferably between 210 and 350°C, and advantageously 230-320°C;
- the pressure is between 0.1 and 25 MPa (10^5 Pa) and preferably between 1.0 and 20 MPa;
- the velocity per unit of volume and per hour (vvh expressed in volume of load injected per unit of volume of catalyst and per hour) is between approximately 0.05 and approximately 100 and preferably between approximately 0.1 and approximately 30 h^{-1} .

The contact between the load and the catalyst is brought about in the presence of hydrogen. The percentage of hydrogen used and which is expressed in liters of hydrogen per liter of load is between 50 and approximately 2000 L of hydrogen per liter of load and preferably between 100 and 1500 L of hydrogen per liter of load.

One of the characteristics of the process according to the invention is that the temperature of the HDF step is lower than the temperature of the catalytic hydrodewaxing (HDPC) step. The difference $T_{HDPC} - T_{HDF}$ is generally between 20 and 200 and preferably between 30 and 100°C.

The effluent leaving the HDF step is sent into the distillation train which integrates atmospheric distillation and vacuum distillation, for the purpose of separating the conversion products with a boiling point lower than 340°C and preferably lower than 370°C, (and including in particular those formed during the catalytic hydrodewaxing (HDPC) step), of the fraction which constitutes the oil base and whose initial boiling point is higher than 340°C and preferably higher than 370°C.

Furthermore, this vacuum distillation section makes it possible to separate the different grades of oils.

The base oils obtained according to this process have a pour point lower than -10°C, a weight content of aromatic compounds less than 2%, a VI greater than 95, preferably greater than 110 and even more preferably greater than 120, a viscosity of at least 3.0 cSt at 100°C, and ASTM color less than 1 and a UV stability such that the increase of the ASTM color is between 0 and 4 and preferably between 0.5 and 2.5. /15

The UV stability test, adapted from the ASTM D925-55 and D1148055 processes, provides a fast method for comparing the stability of the lubricating oils exposed to a source of ultraviolet radiation. The test chamber consists of a metallic enclosure provided with a rotating tray which holds the oil samples. A bulb producing the same ultraviolet radiation as that of sunlight and placed at the top of the test chamber is directed downward onto the samples. Included among the samples is a standard oil with known UV characteristics. The ASTM D1500 color of the samples is determined at $t = 0$ and then after 45 h of exposure at 55°C. The results are transcribed for the standard sample and the test samples as follows:

a) initial ASTM D1500 color,

- b) final ASTM D1500 color,
- c) increase of the color,
- d) turbidity,
- e) precipitate.

Another advantage of the process according to the invention is that it is possible to reach very low aromatic contents, less than 2 wt%, preferably less than 1 wt% and better yet less than 0.05 wt%, and even to go as far as producing white oils of medicinal grade with aromatic contents less than 0.01 wt%. These oils have values of UV absorbency at 275, 295 and 300 nanometers respectively less than 0.8, 0.4 and 0.3 (ASTM D2008 method) and a Saybolt color between 0 and 30.

Particularly advantageously therefore, the process according to the invention also makes it possible to obtain medicinal white oils. The medical white oils are mineral oils obtained by thorough refining of petroleum, their quality is subject to different regulations aiming to guarantee their harmlessness for pharmaceutical applications; they are devoid of toxicity and are characterized by their density and their viscosity. The medicinal white oils essentially contain saturated hydrocarbons, they are chemically inert and their aromatic hydrocarbon content is low. Particular attention is paid to the aromatic compounds and particularly to 6 polycyclic aromatic hydrocarbons (P.A.H. for the Anglo-Saxon abbreviation of polycyclic aromatic hydrocarbons) which are toxic and present in concentrations of one part per billion by weight of aromatic compounds in the white oil. The verification of the total aromatic content can be done by the ASTM D 2008 method; this test of UV adsorption at 275, 292 and 300 nanometers makes it possible to verify an absorbency less than respectively 0.8, 0.4 and 0.3 (that is to say that the white oils have aromatic contents less than 0.01 wt%). These measurements are done with concentrations of 1 g of oil per liter, in a 1 cm vessel. The marketed white oils are differentiated by their viscosity but also by their original crude which can be paraffinic or naphthenic, these two parameters will induce differences

/16

both in the physicochemical properties of the white oils in consideration but also in their chemical composition.

Currently, whether the oil cuts come from direct distillation of a crude oil followed by extraction of the aromatic compounds by a solvent or from a catalytic hydrotreating or hydrocracking process, they still contain non-negligible quantities of aromatic compounds. In the current legislative context of the majority of the industrialized countries, the so-called medicinal white oils must have an aromatic content less than a threshold imposed by the legislation of each country. The absence of these aromatic compounds in the oil cuts is expressed by a Saybolt color specification which must be roughly at least 30 (+30), a maximum UV adsorption specification which must be less than 1.60 at 275 nm based on a pure product in a 1 centimeter vessel and a maximum specification of absorption of the products of extraction by DMSO which must be less than 0.1 for the American market (Food and Drug Administration), standard No. 1211145). The latter test consists of specifically extracting polycyclic aromatic hydrocarbons using a polar solvent, often DMSO, and of verifying their content in the extract by a measurement of UV absorption in the 260-350 nm domain.

The middle distillates obtained have improved pour points (lower than or equal to -20°C), low aromatic contents (at most 2 wt%), polyaromatic (di- and more) contents less than 1 wt%, and for the gas oils, a cetane index greater than 50, and even greater than 52.

Another advantage of the process according to the invention is that the total pressure can be the same in all the reactors, hence the possibility of working in series and of using a single unit and therefore generating cost savings.

/17

The process is illustrated in Figures 1 and 2, Figure 1 representing the treatment of the whole liquid fraction by hydrodewaxing and Figure 2 representing the treatment of a hydrocracking residue.

In Figure 1, the load goes through pipe (1) into hydrotreatment zone (2) (which can be composed of one or more reactors, and can include one or more catalyst beds with one or more catalysts) into which the hydrogen enters (for example, through pipe (3)) and where hydrotreatment step (a) is carried out.

The hydrotreated load is transferred through pipe (4) to hydrocracking zone (5) (which can be composed of one or more reactors, and can include one or more catalyst beds with one or more catalysts) where hydrocracking step (b) is carried out in the presence of hydrogen.

The effluent coming from zone (5) is sent through pipe (6) to tank (7) for separation of the hydrogen which is extracted through pipe (8); the effluent is then distilled at atmospheric pressure in column (9) from which the gaseous fraction is extracted at the top through pipe (10). Step (c) of the process is thus accomplished.

At the bottom of the column, a liquid fraction containing the compounds with a boiling point higher than 340°C is obtained. This fraction is evacuated through pipe (11) to catalytic dewaxing zone (12).

Catalytic dewaxing zone (12) (entailing one or more reactors, one or more catalyst beds with one or more catalysts) also receives hydrogen through pipe (13) for carrying out step (d) of the process.

The effluent leaving this zone through pipe (14) is sent directly to hydrofinishing zone (15) (entailing one or more reactors, one or more catalyst beds with one or more catalysts) from which it emerges through pipe (16). Hydrogen can be added if necessary in zone (15) where step (e) of the process takes place.

The effluent obtained is separated in a distillation train (step f of the process) which besides tank (17) for separating the hydrogen through pipe (18), has atmospheric distillation column (19) and vacuum column (20) which treats the atmospheric distillation residue transferred through pipe (21), residue which has an initial boiling point higher than 340°C.

/18

Obtained as products after the distillations are an oil fraction (pipe 22) and fractions boiling at lower temperatures, such as gas oil (pipe 23), kerosene (pipe 24), gasoline (pipe 25), the light gases being eliminated through pipe (26) of the atmospheric column and the gases being eliminated through column [sic; pipe] (27) by vacuum distillation.

In order not to burden the figure, the hydrogen recycling, from tank (7) towards hydrotreatment and/or hydrocracking, and/or from tank (17) towards dewaxing and/or hydrofinishing, has not been represented.

The references of Figure 1 are seen again in Figure 2. The difference lies in the distillation [of] the effluent coming from hydrocracking step (b) which leaves through pipe (6). After separation of the hydrogen in tank (7), it is separated by atmospheric distillation in column (9) from the gases which are extracted through pipe (10). The distillation is carried out in such a way as to obtain a residue with an initial boiling point higher than 340°C which leaves through pipe (11), and to obtain gas oil (pipe 28), kerosene (pipe 29) and gasoline (pipe 30) fractions.

Only the residue is treated in dewaxing zone (12).

The recycling operations described later are completely transposable.

Diagrammed here is the conversion unit with 2 reactors without recycling of the effluent leaving hydrocracker (5).

It is also possible to recycle a portion of this effluent towards the hydrotreatment step taking place in zone (2) and/or towards the hydrocracking step taking place in zone (5).

The operator will adapt the level of recycling to his "products" objective in order to favor obtaining oils or obtaining middle distillates rather.

The hydrotreatment and hydrocracking zones are also frequently found in the same reactor. The

/19

transfer of the hydrotreated effluent therefore occurs directly without pipe (4). Recycling of the effluent is always possible, either towards the hydrotreatment zone (upstream from a catalyst bed) or towards the hydrocracking zone.

In another embodiment of this conversion step (hydrocracking in two steps), the residue leaving through pipe (11) and which has an initial boiling point higher than 340°C (as shown in Figure 2) is sent, at least in part, to additional hydrocracking zone (32), different from zone (5) (entailing one or more reactors, one or more catalyst beds with one or more catalysts). This other hydrocracking zone can contain the same catalyst as zone (5) or another catalyst.

The resulting effluent is recycled towards the atmospheric distillation step.

The other portion of the residue with an initial boiling point higher than 340°C is transferred towards the catalytic dewaxing step.

These possible modalities for the conversion unit are diagrammed in Figure 3 which again uses the references in common with Figure 2 and which will not be redescribed.

The residue leaving column (9) through pipe (11) is sent to the other hydrocracking zone (32), from which an effluent emerges in pipe (33), which is recycled in column (9). Through pipe (34) connected on pipe (11), the residue leaves and is sent to dewaxing zone (12).

Shown also in Figure 3 is the execution of hydrotreatment zone (2) and hydrocracking zone (5) in the same reactor (31), but separate zones are entirely possible in combination with additional hydrocracking zone (32).

The conversion unit of Figure 3 can thus be substituted for the conversion unit of Figure 2, with the hydrodewaxing, hydrofinishing steps and the distillation train unchanged. All the additional possibilities (H₂ recycling...) are transposable.

In another variant of Figure 2 or 3, the residue leaving pipe (11) is sent to unit (35) for extraction of

/20

the aromatic compounds which is provided with pipe (36) for entrance of the solvent, pipe (37) for exit of the solvent and pipe (38) through which the raffinate is sent to catalytic dewaxing zone (12).

This variant (corresponding to step (c') of the process) is shown in Figure 4. The treatments upstream and downstream are those of the process as illustrated, for example, in Figure 2 or 3.

Thus, the invention also relates to an installation for the production of high quality oils and possibly high quality middle distillates, which has:

- at least one hydrotreatment zone (2) containing at least one hydrotreatment catalyst and provided with at least one pipe (1) for introduction of the load and at least one pipe (3) for introduction of the hydrogen,
- at least one hydrocracking zone (5) containing at least one hydrocracking catalyst, for treating the hydrotreated effluent coming from zone (2), the hydrocracked effluent leaving zone (5) through pipe (6),
- at least one atmospheric distillation column (9) for treating the hydrocracked effluent, and which is provided with at least one pipe (10) for exit of the gaseous fraction, at least one pipe (11) for exit of a liquid fraction (residue) containing the compounds with boiling points higher than 340°C, at least one pipe (28, 29 or 30) for exit of at least one distillate,
- at least one unit (35) for extraction of the aromatic compounds in order to treat the residue, which is provided with at least one pipe (35) [sic: (36)] for introducing the solvent, at least one pipe (36) [sic: (37)] for exit of the solvent, and at least one pipe (38) for exit of the raffinate,
- at least one catalytic dewaxing zone (12) containing at least one dewaxing catalyst, into which the raffinate enters and receives hydrogen through at least one pipe (13), zone (12) being provided with at least one pipe (14) for exit of the dewaxed effluent,
- at least one hydrofinishing zone (15) for treating the dewaxed effluent by a hydrofinishing catalyst, the effluent leaving through at least one pipe (16),

- at least one distillation zone which has at least one atmospheric distillation column (19) and at least one vacuum distillation column (20), column (19) being provided with at least one pipe (26) for exit of the light gases, at least one pipe (23, 24 or 25) for exit of at least one distillate, and at least one pipe (21) for collecting a residue, column (20) having at least one pipe (22) for exit of the oil fraction and at least one pipe (27) for exit of the other compounds. /21

In another embodiment, an installation is described in which zones (2) and (3) are situated in the same reactor provided with at least one pipe (1) for entrance of the load, at least one pipe (3) for entrance of the hydrogen, and at least one pipe (6) for exit of the hydrocracked effluent, said installation moreover having at least one additional hydrocracking zone (32) provided with at least one pipe (11) for introduction of the residue coming from atmospheric distillation column (9), and at least one pipe (33) for exit of the effluent thus hydrocracked, said pipe (33) opening into pipe (6) in order to recycle said effluent, and the installation moreover has at least one pipe (34) situated on pipe (11) for transferring the residue to extraction unit (35).

1. A process for the production of high quality oils and possibly of high quality distillates from a hydrocarbon load of which at least 20 volume % boils at above 340°C, a process which successively entails the following steps:

- (a) hydrotreatment carried out at a temperature of 330-450°C, under a pressure of 5-25 MPa, with a space velocity of $0.1-6 \text{ h}^{-1}$, in the presence of hydrogen in a hydrogen/hydrocarbon volume ratio of 100-2,000, and in the presence of an amorphous catalyst containing at least one metal of group VIII and at least one metal of group VI B,
- (b) hydrocracking, without intermediate separation of the effluent obtained after the hydrotreatment, the hydrocracking being carried out at a temperature of 340-430°C, under a pressure of 5-25 MPa, with a space velocity of $0.1-5 \text{ h}^{-1}$, in the presence of hydrogen, and in the presence of a catalyst containing at least one zeolite and also containing at least one element of group VIII and at least one element of group VI B,
- (c) atmospheric distillation of the effluent obtained after hydrocracking in order to separate the gases from the liquid, and recover at least one liquid fraction which contains compounds with a boiling point higher than 340°C,
- (d) said fraction being treated directly by catalytic dewaxing at a temperature of 200-500°C, under a total pressure 1-25 MPa, with a velocity per unit of volume and per hour of $0.05-50 \text{ h}^{-1}$, with 50-2000 L of hydrogen/L of load, in the presence of a catalyst also containing at least one hydro-dehydrogenating function and at least one zeolite chosen from the group formed by the ZSM-48, EU-2, EU-11 AND ZBM-30 zeolites,
- (e) the dewaxed effluent directly undergoes a hydrofinishing treatment carried out at a temperature of 180-400°C, which is lower than the temperature of the catalytic dewaxing by at least 20°C and

at most 200°C, under a total pressure of 1-25 MPa, with a velocity per unit of volume and per hour of 0.05-100 h⁻¹, in the presence of 50-2000 L of hydrogen/liter of load, and in the presence of an amorphous catalyst for the hydrogenation of the aromatics, containing at least one metal chosen from the group of the metals of group VIII and of the metals of group VI B,

- (f) the effluent coming from the hydrofinishing treatment undergoes a distillation step entailing an atmospheric distillation and a vacuum distillation so as to separate at least one oil fraction with a boiling point higher than 340°C, and which has a pour point lower than -10°C, a weight content of aromatic compounds less than 2%, and a VI greater than 95, a viscosity at 100°C of at least 3 cSt (or 3 mm²/s), and so as to separate possibly at least one middle distillate fraction with a pour point lower than or equal to -20°C, an aromatic content of at most 2 wt% and a polyaromatic content of at most 1 wt%.

/23

2. A process according to one of the preceding claims, in which the hydrofinishing catalyst of step (e) entails an amorphous support, at least one noble element of group VIII, chlorine and fluorine.

3. A process according to one of the preceding claims, in which hydrotreatment step (a) and hydrocracking step (b) are carried out in the same reactor.

4. A process according to one of the preceding claims, in which hydrotreatment step (a) and hydrocracking step (b) are carried out in different reactors.

5. A process according to one of the preceding claims, in which, in atmospheric distillation step (c), a residue with an initial boiling point higher than 340°C is obtained and then undergoes the catalytic dewaxing of step (d).

6. A process according to Claim 5, in which the hydrocracking residue is recycled at least in part in the hydrotreatment step and/or in the hydrocracking step.

7. A process according to Claim 5, in which at least a portion of the hydrocracking residue undergoes an additional hydrocracking step different from step (b), the effluent obtained being recycled towards atmospheric distillation step (c), the other portion of the residue being treated in dewaxing step (d).

8. A process according to one of Claims 5 to 7, in which the residue coming from the atmospheric distillation of step (c) undergoes extraction of the aromatic compounds (step c'), and the raffinate obtained is catalytically dewaxed in step (d).

9. A process according to one of the preceding claims for the production of white oils with aromatic contents less than 0.01 wt%.

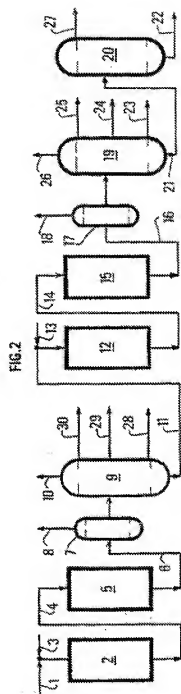
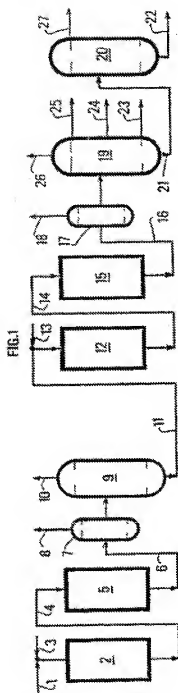


FIG.3

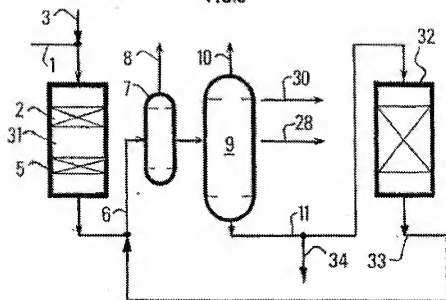
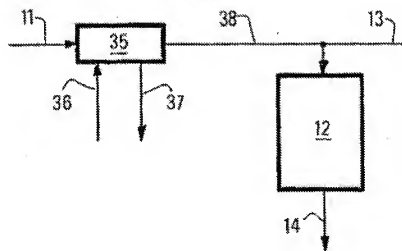


FIG.4



PCT/FR 01/01221

According to International Patent Classification (IPC) or to both national classification and IPC

IPC 7 C106

Documentation researchers make their relevant documentation to the extent that such documents are included in the fields named in the following list:

Electronic data base generated during the information search process of data base and, whose practical search forms used

EPC-internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Citation:	Citation of document, with indication, where appropriate, of the relevant passages
-----------	--

Endorse to claim No.

X WD 98 02503 A (CHEVRON USA INC)
22 January 1998 (1998-01-22)
page 15, line 9; claims 1-39
page 23, line 19 -page 24, line 10
page 26, line 5 - line 8

1-9

A US 5 468 368 A (BAKER JR CHARLES L ET AL)
21 November 1995 (1995-11-21)
the whole document.

1-9

A US 4 347 121 A (MAYER JEROME F ET AL)
31 August 1982 (1982-08-31)
column 3, line 9 -column 5, line 61;
example 9

1-9

A US 5 358 627 A (MEARS DAVID E ET AL)
25 October 1994 (1994-10-25)

no/yes

Y Further documents are listed in the continuation of box C.

Y **Parents family members are listed in annex**

* Special categories of card documents:

*A document defining the general state of the art which is not considered to be of particular relevance

E earlier document not published on or after the international filing date

* document which may throw doubt on validity, timing or which is cited in evidence; the publication date or another relation or other special reason (as specified)

*D' declared relating to an oral disclosure, use, exhibition or other means.

P document published prior to the International Copyright but later than the priority date claimed

* later document published after the International filing date or priority date and not in conflict with the application but often in accordance with the principle or theory underlying the invention.

*X deemed of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is considered with one or more other such documents, such combination being obvious to a person skilled

2 ထိုသို့အားဖြင့် အကယ်၍ ခုနစ် အသက် ပေါက်ကွဲသွားပါက

Date of the second completion of the international source

Order of making of the international research report

13 July 2001

20/07/2001

Name and mailing address of the ISA
European Patent Office, P.O. 5815 Finkenheims 2
M. - 2250147 Nijmegen
Tel. (+31-70) 340-2240, Tx. 31 657 090 nl
Fax: (+31-70) 340-2016

Authorized officer

Michiels, P.

From: COT/02/0218 (Respondent's Only) 09/02/2002

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/FR 01/01221

C/(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Number of documents, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 10578 A (FINA RESEARCH ;GROOTJANS JACQUES FRANCOIS JEA (BE); AKZO NOBEL NV) 20 April 1995 (1995-04-20) the whole document	1-9
A	EP 0 590 672 A (MITSUBISHI OIL CO) 6 April 1994 (1994-04-06) page 3, line 27 -page 4, line 31	1-9
P,A	FR 2 785 616 A (INST FRANCAIS DU PETROL) 12 May 2000 (2000-05-12) the whole document	1-9

Form PCT/ISA(2010) Confirmation of documents (July 2010)

page 2 of 2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/FR 01/01221

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9802503 A	22-01-1998	AU 724363 B	21-09-2000
		AU 3664997 A	09-02-1998
		BR 9710326 A	17-08-1999
		CZ 9900096 A	14-04-1999
		EP 0912660 A	06-05-1999
		HU 0094280 A	28-04-2001
		JP 2000515185 T	14-11-2000
		PL 331037 A	21-06-1999
		TR 9900097 T	22-03-1999
US 5468368 A	21-11-1995	AU 696408 B	10-09-1998
		AU 7110194 A	17-01-1995
		CA 2165656 A	05-01-1995
		DE 69423213 D	06-04-2000
		DE 69423213 T	09-11-2000
		EP 0705321 A	10-04-1996
		ES 2142948 T	01-05-2000
		JP 8511828 T	10-12-1996
		SG 42998 A	17-10-1997
		WO 9500604 A	05-01-1995
US 4347121 A	31-08-1982	NONE	
US 5358627 A	25-10-1994	NONE	
WO 9510578 A	20-04-1995	SG 48993 A	18-05-1998
		AT 153519 T	15-08-1997
		AU 683938 B	27-11-1997
		AU 7812594 A	04-05-1996
		BR 9407765 A	18-03-1997
		CA 2173599 A	20-04-1995
		CN 1132522 A,B	02-10-1996
		CZ 9600991 A	11-09-1996
		DE 69404320 D	21-08-1997
		DE 69404320 T	29-01-1998
		EP 0722478 A	24-07-1996
		ES 2105762 T	16-10-1997
		FI 961532 A	04-04-1996
		HU 75022 A,B	28-03-1997
		JP 9603541 T	08-04-1997
		KR 199849 B	15-06-1999
		NO 961379 A	03-04-1996
		PL 313868 A	22-07-1996
		RU 2128681 C	10-04-1999
		US 5935414 A	10-08-1999
EP 0590672 A	06-04-1994	JP 3065816 B	17-07-2000
		JP 6110571 A	26-04-1994
		AU 666973 B	29-02-1996
		AU 4877493 A	14-04-1994
		CA 2107375 A	03-04-1994
		SG 46339 A	20-02-1998
		US 5462650 A	31-10-1995
FR 2785616 A	12-05-2000	FR 2785617 A	12-05-2000
		WO 0027950 A	18-05-2000

None PCT/FR 01/01221 Patent family across (Only when)